

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
23 December 2004 (23.12.2004)

PCT

(10) International Publication Number
WO 2004/110719 A2

(51) International Patent Classification⁷: **B29C 41/00**

(21) International Application Number:
PCT/IB2004/002420

(22) International Filing Date: 14 June 2004 (14.06.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/478,778 16 June 2003 (16.06.2003) US

(71) Applicants and

(72) Inventors: **EDERER, Ingo** [DE/DE]; Feuerhausstrasse
3, 82269 Geltendorf (DE). **HÖCHSMANN, Rainer**
[DE/DE]; Schlossstrasse 16, 86682 Genderkingen (DE).

(74) Agent: **WAGNER, Sigrid**; Steinsdorfstrasse 5, 80538
München (DE).

(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,
SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished
upon receipt of that report*

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: IMPROVED METHODS AND SYSTEMS FOR MANUFACTURE OF LAYERED THREE-DIMENSIONAL FORMS

(57) Abstract: Improved Methods and Systems for the Manufacture of Layered Three-Dimensional Forms New methods and sys-
tems for manufacturing a three-dimensional form, comprising steps of providing a plurality of particulates; contacting the particulates
with an activation agent; contacting particulates having the activation agent with a binder material that is activatable by the activation
agent; at least partially hardening the binder for forming a layer of the three-dimensional form; and repeating these steps to form
the remainder of the three-dimensional form. Following sequential application of all required layers and binder material to make the
form, the unbound particles are appropriately removed (and optionally re-used), to result in the desired three-dimensional form. The
invention also contemplates a novel method for preparing a form, where unbound particulates free of binder material are re-claimed.



WO 2004/110719 A2

Improved Methods and Systems for the Manufacture of Layered Three-Dimensional Forms

Technical Field

5

[0001] The present invention relates to the manufacture of three-dimensional forms and more particularly relates to the manufacture of a three-dimensional form by the successive layer-by-layer build up of a composite including particles in a hardened binder material.

10

Background of the Invention

[0002] The present invention is predicated upon the discovery of improvements to materials and techniques useful for a process that has gained recognition in the art as "three-dimensional printing". A number of efforts in this field have been made to date, including by way of example those disclosed in U.S. Patent Nos. 6,147,138, 6,193,922, 6,423,255, 6,416,850, 6,375,874, 6,007,318, 5,204,055, 5,340,656, 5,387,380, 5,490,962, 5,518,680, 5,902,441 and PCT Application Nos. WO 02/26420 (PCT/DE01/03661), WO 02/26478 (PCT/DE01/03662), WO 02/28568 (PCT/DE01/03834), WO 02/26419 (PCT/DE00/03324), and WO 02/083323 (PCT/DE02/01103), all of which are hereby expressly incorporated by reference.

[0003] By way of illustration, U.S. Patent No. 5,204,055 addresses a method that includes layer based deposition of untreated particulated material. A binder material is liquid dosed to selectively bind the particles. The binder is hardened and the part is unpacked. The patent is limited in its teachings with regard to sequencing for contacting of particles with agents for binding the particles.

[0004] In WO96/05038, there is disclosed a method for production of bone implants including mixing a powder with a binder, layer based deposition, selectively laser sintering or selectively spraying an agent on top of each layer to bind the particles. The document likewise is limited in its

teachings with regard to sequencing for contacting of particles with agents for binding the particles.

[0005] In U.S. Patent No. 6,416,850, there is described a method whereby certain purported non-toxic materials characterized as adhesives (e.g., water soluble polymers and carbohydrates) are mixed with particles and other ingredients and selectively aggregated by depositing a solvent in which the adhesive is highly soluble. The patent is limited in its teachings with regard to sequencing for contacting of particles with agents for binding the particles. Additionally, it is believed to not enable a process where agents are cross-linked for assisting in bonding, particularly to make a form sufficiently strong and thermal resistant to serve as a mold.

[0006] It is thus an objective of the present invention to provide improved and efficient alternatives for preparing a three-dimensional form with a layer-by-layer build-up technique, particularly through the use of a binding material system that is at least two components.

Summary of the Invention

[0007] Accordingly, the present invention is predicated upon the discovery of a new method for manufacturing a three-dimensional form, comprising the steps of providing a plurality of particulates; contacting at least a portion of a surface of the particulates with an activation agent; contacting a pre-selected portion of the particulates having the activation agent with a binder material that is activatable by the activation agent; hardening the binder for forming a layer of the three-dimensional form; and repeating these steps to form the remainder of the three-dimensional form. Following the sequential application of all of the required layers and binder material to form the part in question, the unbound particles are appropriately removed (and optionally re-used), resulting in the formation of the desired three-dimensional form.

[0008] Preferably the binder material is selectively supplied to the particulates (e.g., by using an ink-jet printing technique, or other suitable technique for precise fluid dispensing), in accordance with a computer model of the three-dimensional part being formed, such as from the use of a Computer Aided Design (CAD) file (e.g., CAD file data that results from a

finite element analysis). In this manner predefined sub-areas of each layer can be varied relative to adjoining layers. The agent is adapted to effectively create a binder for firmly coupling adjoining particles, whether by Van der Waals forces, cross-linking, other covalent bonding, ionic bonding, metallic bonding, combinations thereof or by another mechanism).

[0009] According to a particularly preferred approach of the present invention, each layer of the form being manufactured is initially provided as a layer including a plurality of particulates in the absence of a binder material. Preferably, the binder material is dispensed by a suitable fluid dispenser into the respective sub-areas of a layer whereupon it contacts an activation agent and is activated for hardening to form a matrix that has the particles firmly held within it.

[0010] Though it is contemplated that the binder material and the activation agent may be dispensed individually onto a layer of particles, or that particles may be dispensed onto a layer, film or other area of activation agent, it is most preferred that the binder material is dispensed onto a sub-area of a layer of particles that are contacted, prior to dispensing of the binder material with an activation agent.

[0011] It is thus found that a number of benefits are possible using the methods of the present invention. By way of example, it is possible to better manage material usage and reduce overall cost by improving control over the total amount of binder that is used (which in many instances is desirably a thermoset or crosslinkable resin that may require special handling or waste disposal). Further, the absence of a binder makes it possible to more efficiently reclaim and re-use particles in subsequent fabrications. That is, the particles will be substantially free of binder material that could preclude further use of the particles.

[0012] Thus, an advantageous method for making a three dimensional form could comprise the steps of providing a plurality of particulates; contacting at least a portion of a surface of the particulates with a multiple-component binder material system including a binder material as one of the components; hardening the binder for forming a layer of the three-dimensional form; repeating the steps to form the remainder of the three-dimensional form;

and re-claiming unbound particulates, said unbound particulates being free of binder material.

[0013] In addition, it is possible to reduce the potential for nozzle clogging. It is also found that good control over the extent unreacted binder material is possible to help minimize a potential source of gas formation, which is potentially problematic in some applications (e.g., where the three-dimensional form is used as a mold for casting a high melting point material and the mold is highly complex, such as with a automotive cylinder head mold or another intricate form). The present invention affords good control over binder deposition and permits for high degrees of variations within a layer and within cross-sections of the form.

[0014] The present invention also affords other benefits. For example, in one particularly preferred aspect of the present invention, functional groups or reactive components of the binder material are susceptible to evaporation, especially at higher temperatures. The ability to better control and even delay when the binder material is going to be contacted with particles helps to assure that a greater effective amount of the functional groups or reactive components will be present over time. Thus, consumption of overall amounts of the binder material can be further reduced, as compared with a process in which the binder material is contacted initially with particles, prior to the activation agent. To illustrate, if furane resin is employed as a binder for a sand, it is more likely that at higher temperatures, the furfurylic alcohol of the resin will evaporate at higher temperatures. That means the sand has to be used very quick (e.g., within minutes) after mixing with the furane resin, or else the sand must be sealed, in order to preserve the efficacy of the binder material. On the other hand, if the sand is contacted with activation agent first, the activation agent (e.g., an acid such as sulfuric acid that is relatively stable at normal operating conditions) will very often not be susceptible to substantial effects of temperature or atmosphere. Thus, enhanced particle stability permits for longer delays between steps, as well as the introduction of additional intermediate processing steps. Delays between steps of 2 hours or more, or as long as 12 hours are also possible, without compromising particle reactivity or stability. In one preferred embodiment, particles contacted with an activation agent as disclosed herein can await 24 hours or more and remain

free of degradation to binding function, in the absence of contacting with a binder material.

[0015] It is also likely that there will be fewer adverse secondary effects caused by evaporation of functional groups or reactive components. For example, the susceptibility of the evaporated materials to re-deposit elsewhere within the system (e.g., on the print head) is reduced. This leads to longer system component cleaning cycles, which again increases the productivity.

[0016] The present invention also contemplates kits for supplying the necessary consumable materials to carry out the preferred methods. For example, one such kit for preparing a three-dimensional form, may include a first container including a binder material, and a second container including a particulated material and an activation agent for the binder material.

15 Detailed Description of the Preferred Embodiment

[0017] The present invention is predicated upon the discovery of a new method for manufacturing a three-dimensional form, comprising the steps of providing a plurality of particulates; contacting at least a portion of a surface of the particulates with an activation agent; contacting a pre-selected portion of the particulates having the activation agent with a binder material that is activatable by the activation agent; hardening the binder for forming a layer of the three-dimensional form; and repeating these steps to form the remainder of the three-dimensional form.

[0018] In an especially preferred aspect, though not intended as a limitation of the scope and applicability of the invention, the invention contemplates a method for manufacturing a mold comprising the steps of providing a plurality of particulates; contacting at least a portion of a surface of the particulates with an activation agent for causing cross-linking of an organic binder material; depositing the binder material onto a pre-selected portion of the particulates; hardening the binder for forming a layer of the mold; and repeating these steps to form the remainder of the mold.

[0019] The particles of the present invention may be any suitable finely divided material that is capable of being bonded to form an aggregate with an

activated binder. The particles may be organic, inorganic, or a mixture thereof. They may be ceramic, metal, plastic, carbohydrate, small organic molecule, large organic molecule, combinations thereof or the like.

5 **[0020]** Preferably the particles are generally mono-disperse. Thus, the particles preferably have at least 80 percent by volume of an average particle size ranging from about 30 μm to about 450 μm , more preferably about 90 μm to about 210 μm , and still more preferably on the order of 140 μm . Polydisperse collections of particles are also possible. Larger and smaller particle sizes are also possible and the above ranges are not intended as
10 limiting of the invention.

[0021] A highly preferred material for use as the particles of the present invention, particularly for use in the manufacture of molds, is sand, and more particularly foundry sand. Examples of suitable sands include silica. In a more preferred aspect the sand is selected from the group consisting of quartz,
15 zircon, olivin, magnetite, or combinations thereof. Sands may be virgin sand, reclaimed sand, or a combination thereof. The sands may also include ingredients common to foundry sand such as a binder (e.g., clay, wood flour, chemical additives, etc.), carbonaceous additives, or other ingredients.

[0022] It will be appreciated from the above, that sand particles are not
20 the only particles useful in the present invention. Other art-disclosed particles may be employed, such as cera beads, metal particles, ceramic particles, polymeric particles, combinations thereof or the like.

[0023] The binder of the present invention may be any suitable material that is capable of firmly coupling adjoining particulates to each other. In a
25 highly preferred aspect, the binder material is an organic compound, and more particularly an organic compound that includes molecules that cross-link or otherwise covalently bond among each other.

[0024] In a highly preferred embodiment, the preferred material for the binder includes at least one material selected from the group consisting of
30 phenol resin, polyisocyanate, polyurethane, epoxy resin, furane resin, polyurethane polymer, phenolic polyurethane, phenol-formaldehyde furfuryl alcohol, urea-formaldehyde furfuryl alcohol, formaldehyde furfuryl alcohol, peroxide, polyphenol resin, resol ester or mixtures thereof.

[0025] Though other viscosities are possible, during dispensing through a print head, preferably, the viscosity of the binder material at 20° C. preferably ranges from 5 to about 60 cps, and more preferably 10 to 50 cps, and still more preferably about 14 to about 20 cps.

5 **[0026]** It may also be possible to employ one or more inorganic binders such as, without limitation a silicate (e.g., sodium silicate), a salt, plaster, bentonite or mixtures thereof.

10 **[0027]** Other art-disclosed ingredients may also be employed to form a binder in the present invention, such as those disclosed in U.S. Patent No. 6,416,850, hereby incorporated by reference, including for example water-soluble polymers, carbohydrates, sugars, sugar alcohols, or proteins. Suitable water-soluble polymers include polyethylene glycol, sodium polyacrylate, polyvinyl alcohol, polyvinyl pyrrolidone, sodium polyacrylate copolymer with maleic acid, and polyvinyl pyrrolidone copolymer with vinyl acetate;
15 carbohydrates include acacia gum, locust bean gum, pregelatinized starch, acid-modified starch, hydrolyzed starch, sodium carboxymethylcellulose, sodium alginate and hydroxypropyl cellulose. Suitable sugars and sugar alcohols include sucrose, dextrose, fructose, lactose, polydextrose, sorbitol and xylitol. Organic compounds including organic acids and proteins can also
20 be used, including citric acid, succinic acid, polyacrylic acid, gelatin, rabbit-skin glue, soy protein, and urea. Thus it is contemplated that the binder may include a binding component that is free of a thermoset resin.

25 **[0028]** The activation agent of the present invention is preferably an ingredient that in the presence of the binder material (and optionally in the presence of another controllable atmospheric condition, e.g., heat, moisture, or otherwise), will cause the binder material to bond to itself and to adjoining particles. The activation agent is preferably provided as a solid, liquid, gel, or combination thereof. It may include an art-disclosed curing agent, initiator, or both for the above mentioned binder materials.

30 **[0029]** For example, in one particularly preferred embodiment, (e.g., where a furane resin, epoxy or both is employed), the activation agent is an agent selected from an acid, an amine, an ester or a combination thereof. Preferred acids, for example, are those having a pH of from 1 to 6, and more preferably less than 4. Examples of suitable acids include organic acids,

inorganic acids, or combinations thereof, such as one or more acids selected from the group consisting of sulfuric acid, sulfonic acid (e.g., methanesulfonic acid, toluenesulfonic acid or the like), hydrochloric acid, phosphoric acid, hydrochloric acid, and nitric acid. The activation agent may be a relatively low viscosity material or a relatively high viscosity material. Thus, it is also contemplated that a dimer or trimer acid, a fatty acid, or combinations thereof may be employed. Other acids are also contemplated, including without limitation, (poly)carboxylic acids,

5
10 **[0030]** The activation agent may consist of a single ingredient or a plurality of ingredients. For example, as taught in U.S. Patent No. 6,423,255, the curing agent may comprise toluene sulfonic acid in a proportion of 45 to 55 percent, diethylene glycol in a proportion of 5 to 15 percent, and sulphuric acid in a proportion of at most 1 percent.

15 **[0031]** Suitable amines are selected from primary amines, secondary amines, tertiary amines, or combinations thereof. For example, without limitation, the amine may be selected from the group consisting of aliphatic amines, aromatic amines, polyoxyalkyleneamines, phenalkamines, alkyl amines, alkylene amines, combinations thereof, or the like.

20 **[0032]** To the extent not already mentioned, other art disclosed curing agents may also be employed, such as catalytic curing agents (e.g., boron-containing complexes or compounds), amides, polyamides.

25 **[0033]** It is also possible that the activation agent may be such that it becomes active upon the liberation of a gas (e.g., a dioxide, such as carbon dioxide, sulfur dioxide) from within it. Thus, such a preferred activation agent preferably is one that is capable of liberating such a gas in the presence of the binder material.

30 **[0034]** Of course, other activation agents are also possible. For example, as described in U.S. Patent No. 6,416,850, hereby incorporated by reference, an activating fluid may be employed, such as a solvent selected from water, methyl alcohol, ethyl alcohol, isopropyl alcohol, acetone, methylene chloride, acetic acid, and ethyl acetoacetate.

[0035] The skilled artisan will appreciate that in certain embodiments it may also be desirable to include one or more additional components such as to assist in processing of the materials, to improve a property of a material, or

otherwise. Thus, it is further contemplated that in addition to the particles, binder and activation agent, there might be employed a filler, a reinforcement, a curing accelerator, a surfactant, a thickener, adhesion promoters, dyes, thermal indicators, humectants, combinations thereof or the like. Examples of fillers include, without limitation, mineral fillers, starches (e.g., maltodextrin), combinations thereof or the like. Reinforcements might include metal, plastic (e.g., aramid, polyester, cellulose, derivatives thereof or the like), ceramic, graphite, carbon or combinations thereof, and may be in the form of whiskers, fibers, combinations thereof or the like.

10 **[0036]** Other art-disclosed ingredients may include, for example, lecithin, a polyol (e.g., polyethylene glycol or polypropylene glycol), citronellol, an acetate (e.g., ethylene glycol diacetate), a sulfate (e.g., potassium aluminum sulfate), a sulfonate, an alcohol, an ether, a (meth)acrylate, a (meth)acrylic acid, a polyvinyl pyrrolidone, or combinations thereof.

15 **[0037]** It should be appreciated that any of the liquid ingredients herein may further contain additional ingredients, such as diluents (e.g., water, a ketone, or another organic solvent (e.g., toluene or the like)).

20 **[0038]** In a particularly preferred aspect of the present invention, a three-dimensional form is prepared using a layer-by-layer build-up approach, pursuant to which binder material is contacted with particles no earlier than when the binder material first contacts the activation agent. Thus, it is possible that both the binder material and the activation agent are supplied simultaneously to the particles (which are optionally pre-contacted with the activation agent). More preferably, the particles are mixed in intimate contact with the activation agent, spread over a surface and then selectively contacted in sub-areas (which can be from a small portion to the entirety of the mass of material) with the binder material.

25 **[0039]** Under the latter approach, mixing may be done in any suitable manner, and may be done by a batch mixer, a continuous mixer or a combination thereof. Preferably, the particles are mixed for a sufficient time so that a coating is developed over at least a portion of the exposed surface of the particle (which the skilled artisan should appreciate may be fully dense or porous). By way of example, without limitation a batch of about 1 to 25 kg (more preferably about 10 kg) is loaded into a rotating mixer along with an

activation agent and rotated for a desired amount of time (e.g., sufficient to develop a layer around the particle to enlarge it to a diameter of about 0.25 to about 2.5 times the uncoated particle diameter, and more preferably about 1.5 times the uncoated particle diameter).

5 **[0040]** The premixed particles are then suitably transported to a work site, such as by a suitable conveyor (e.g., a screw conveyor). It is then loaded onto a work surface (e.g., via a spreading mechanism, such as in WO 02/083323 (PCT/DE02/01103), hereby incorporated by reference) or more preferably to a temporary holding container.

10 **[0041]** The work surface is preferably a workpiece platform of a suitable system for forming three-dimensional forms. An example of a suitable job box for carrying a work surface is disclosed in WO 02/26478 (PCT Application No. PCT/DE01/03662), hereby incorporated by reference. See also U.S. Patent No. 6,423,255, hereby incorporated by reference.

15 **[0042]** A preferred system includes a binder fluid dispenser into which binder is supplied in a fluid state, a work surface upon which a plurality of particles may be loaded, such as particles contacted with an activation agent for the binder, a mechanism for spreading particulated material (e.g., a spreading mechanism includes an oscillating blade, a doctor blade, a counter
20 rotating roller, or a combination thereof); and a processor for commanding the binder fluid dispenser to dispense the binder fluid according to data from a computer-derived model. Preferably, the binder fluid dispenser and the work surface are adapted for translation about at least three axis. For example, the binder fluid dispenser (preferably a drop-on-demand dispenser, such as an
25 ink-jet type dispenser) might have one or a plurality of nozzles translatable in the x-y Cartesian plane, with the work surface being translatable in the z-axis. Either or both of the binder fluid dispenser nozzles or the work surface (e.g., as part of a gantry) may additionally or alternatively be rotatable about an axis.

30 **[0043]** Examples of a spreading mechanisms are described, without limitation, in WO 02/083323 (PCT/DE02/01103), or WO 02/26420 (PCT Application No. DE01/03661), both hereby expressly incorporated by reference. Accordingly, a preferred spreading mechanism includes a movable (e.g., oscillatable) hopper, into which particles are loaded. The hopper has an

opening, such as a slit at the bottom, through which particles can be dispensed when the hopper is moved. A smoothing device (e.g., a blade, counter roller or the like) is preferably attached adjacent the hopper opening. As particles are released through the opening, they are thus smoothed by the smoothing device. In this manner, a relative flat and smooth build-up of a layer of particles is possible on the work surface. Layer thicknesses may be controlled as desired. For example, layers may range in thickness from about 0.05 mm to about 1 mm are formed, and more preferably about 0.1 mm to about 0.4 and still more preferably about 0.15 to about 0.3 mm. Smaller or larger thicknesses are also possible.

[0044] It is possible that the system may also an overflow cavity defined in it for receiving excess material, and possibly a movable cleaning element to transfer excess material to the overflow cavity. A separate partially sealed clean area may also be employed in combination with a work area. Thus, a system of the type disclosed in U.S. Patent No. 6,375,874, hereby expressly incorporated by reference, may also be employed.

[0045] After particles are spread, they are selectively contacted with the binder material. Preferably the binder material is dispensed through at least one binder fluid dispenser, and preferably one characterized in that it employs piezoelectric jets (e.g., as described in U.S. Patent No. 6,460,979, hereby incorporated by reference), a continuous jet spray, an intermittent jet spray, dispenses through a mask, includes a single dispensing nozzle, includes a plurality of dispensing nozzles that are clustered together, includes a heated nozzle, includes a plurality of dispensing nozzles that are spaced apart, or combinations of at least two of the foregoing characteristics.

[0046] Though a variety of other print heads may be employed, in a particularly preferred embodiment, a piezo bending transducer drop-on-demand print head is employed. One or a plurality of transducers is subjected to a triggering pulse to achieve drop discharge movement. It is also possible that, in a plural transducer head, and, each piezo bending transducer neighboring the piezo bending transducer triggered by the triggering pulse is subjected to a compensating pulse deflecting it. See also, U.S. Patent No. 6,460,979, hereby incorporated by reference.

[0047] A preferred droplet density for dispensing fluids through a print head ranges from about 50 dpi to about 1000 dpi. A droplet line density ranging from 100 to 600 dpi is particularly preferred. Higher or lower densities are also possible. For example, a typical dispensing nozzle may range from
5 about 20 to about 100 microns, more preferably about 30 to about 80 microns, and still more preferably about 50 to about 60 microns. Accordingly, droplet diameters less than about 100 microns, more preferably less than 60 microns are possible (it being recognized that a 60 micron diameter corresponds generally with a droplet volume of about 80 pL), and diameters as low as about
10 10 microns or smaller are also possible. Droplet ejection frequency may be varied as desired, but preferably it will be at least 1 Hz, more preferably at least 5 Hz. In one embodiment a frequency of 15 Hz or higher is possible.

[0048] The relative amounts of binder to activation agent materials may be selected and varied as desired. In one embodiment, the relative amount (in
15 parts by weight) of binder to activation agent is about 1: 10 to about 10:1, and more preferably it is about 1:4 to about 4:1. Still more preferably the amount of binder to activation agent is about 2:1. For example, in one preferred embodiment employing a furane resin and sand, a mixture will preferably include about 0.3 weight percent of the activation agent and about 0.6 weight
20 percent of the binder.

[0049] Overall, it is preferred to use less than about 25%, more preferably less than 10% and still more preferably less than 2% by weight overall of a binder in a form that includes particles, binder and activation agent. Of course, higher or lower amounts are also possible.

[0050] To assist in curing of or otherwise hardening the binder material one or more additional stimuli may be employed, including without limitation
25 heat, infrared radiation, ultraviolet radiation, moisture, air, a vacuum, an inert environment, a reactive gas environment, catalysis, combinations thereof, or the like.

[0051] In this regard, the hardening may be performed in a separate enclosed chamber to assure a particular environment. It may also be enhanced such as by heating the work surface of the system, by heating the binder material prior to dispensing (e.g., while it is in a container), during
30 dispensing (e.g., by providing a heated dispensing head, nozzle or both), or

following dispensing. A preferred temperature range for facilitating curing of the binding material is about 15°C to about 40°C, and more preferably about 20°C to about 30°C (e.g., for a furane resin it preferably cures at ambient room temperature). However other resins with a curing point at higher
5 temperature levels are also possible to use, and therefore higher temperatures (or possibly lower temperatures may also be employed).

[0052] Examples of additional techniques that may suitably be employed in the present invention include those disclosed, without limitation, in U.S. Patent No. 6,147,138 (hardened using one or a combination of heat or
10 a reactive gas atmosphere), 6,423,255; WO 02/26419 (addressing hardening selectively dosed binder in a reactive gas atmosphere).

[0053] Further, in some applications, it may be desirable to also remove the three-dimensional form from surrounding bound particle material. Any suitable process may be employed, such as that in WO 02/28568 (PCT
15 Application No. PCT/DE01/03834), hereby expressly incorporated by reference.

[0054] Additional variations are also possible. For example, compositions of particles, binder material, activation agent, or any combination thereof may be constant throughout a form, or it may vary as
20 between two or more different layers.

[0055] In addition, it may be possible to employ a silk screening step in delivering the binder material to a layer of particles, such as by using techniques discussed in U.S. Patent No. 6,193,922, hereby incorporated by reference.

[0056] For one embodiment, one particularly preferred material system furane resin, which preferably contains furfuryl alcohol in a proportion of at least 50 per cent and ethane diol in a proportion of approximately 4 per cent as well as water, is preferably used as binding material. The preferred curing agent contains toluene sulfonic acid in a proportion of 45 to 55 per cent,
25 diethylene glycol in a proportion of 5 to 15 per cent and sulphuric acid in a proportion of at most 1 per cent. For this embodiment, the preferred binder material and the preferred curing agent are preferably used in a ratio of weight of 2:1.
30

[0057] The present invention is useful for and is contemplated for use in a method for making any of a variety of different three dimensional forms, such as those selected from the group consisting of a casting mold (e.g., for metal castings, lost-foam castings, casting that have hollow internal portions that require an internal mold core part, ceramic castings, metal matrix composite castings, or any other castings), a die for molding (e.g. blow molding, rotational molding, injection molding), a die for thermoforming, an extrusion die, an orthopedic implant, a dental restoration, a vascular tissue, a sustained release drug form, a monochromatic prototype part, a multi-colored prototype part, a sculpture, a gradient index lens, a hollow part (e.g., a hollow metal part), an electronics component, a cutting tool (e.g., a ceramic tool such as a tungsten carbide tool or other carbide tool), and a metal matrix composite. The present invention also contemplates articles that are prepared according to the methods herein. For example articles of the invention include a plurality of layers that include particles bound together by a binder material system that is at least two components, including an activation agent and a binder material, wherein the binder material is not contacted with the particles prior to the activation agent.

[0058] The invention finds particularly attractive utility in the manufacture of molds for casting of metals. Without limitation, examples of the use of the methods of the present invention include the formation by metal casting with a mold prepared by the methods herein of an automotive vehicle component (e.g., a cylinder head, a wheel, a powertrain component, a suspension component, a housing, or otherwise).

[0059] It will be further appreciated that functions or structures of a plurality of components or steps may be combined into a single component or step, or the functions or structures of one step or component may be split among plural steps or components. The present invention contemplates all of these combinations.

[0060] It is understood that the above description is intended to be illustrative and not restrictive. Many embodiments as well as many applications besides the examples provided will be apparent to those of skill in the art upon reading the above description. The scope of the invention should, therefore, be determined not with reference to the above description, but

should instead be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. The disclosures of all articles and references, including patent applications and publications, are incorporated by reference for all purposes.

5

CLAIMS

What is claimed is:

- 1) A method for manufacturing a three-dimensional form,
5 comprising:
 - a) providing a plurality of particulates;
 - b) contacting at least a portion of a surface of the particulates with an activation agent;
 - c) contacting a pre-selected portion of the particulates having the
10 activation agent with a binder material that is activatable by the activation agent;
 - d) at least partially hardening the binder for forming a layer of the three-dimensional form; and
 - e) repeating the steps (a)-(d) to form the remainder of the three-
15 dimensional form.
- 2) The method of claim 1 wherein the particulates are selected from the group consisting of a ceramic, a metal, a plastic, a carbohydrate, a
20 small organic molecule, a large organic molecule, combinations thereof or the like.
- 3) The method of claim 1 or 2 wherein the activation agent is selected from the group consisting of acids, amines, alcohols, ketones, salts,
25 or mixtures thereof.
- 4) The method of any of claims 1 through 3 wherein the binder material is selected from the group consisting of binder is at least one material selected from the group consisting of phenol resin, polyisocyanate,
30 polyurethane, epoxy resin, furane resin, polyurethane polymer, phenolic polyurethane, phenol-formaldehyde furfuryl alcohol, urea-formaldehyde furfuryl alcohol, formaldehyde furfuryl alcohol, peroxide, polyphenol resin, resol ester, a silicate (e.g., sodium silicate), a salt, plaster, bentonite, water-

soluble polymers, organic acid, carbohydrates, sugars, sugar alcohols, or proteins.

5 5) The method of any of claims 1 through 4 wherein heat is applied prior to or during the hardening step.

 6) The method of any of claims 1 through 5 wherein the activation agent contacting step (b) is done by a step selected from brushing, rolling, blading, spraying, plating or a combination thereof.

10

 7) The method of any of claims 1 through 6 wherein the contacting step (c) includes dispensing the binder material through a drop-on-demand dispenser.

15 8) The method of any of claims 1 through 7 wherein the viscosity of the binder material at 20° C. preferably ranges from 5 to 60 cps.

 9) The method of any of claims 1 through 8, further comprising a step of re-using particulates that are not contacted with the binder material.

20

 10) The method of any of claims 1 through 9 wherein the three dimensional form is selected from the group consisting of a casting mold, a die for molding, a die for thermoforming, an extrusion die, an orthopedic implant, a dental restoration, a vascular tissue, a sustained release drug form, a monochromatic prototype part, a multi-colored prototype part, a sculpture, a gradient index lens, a hollow part, an electronics component, a cutting tool, and a metal matrix composite.

 11) A method for manufacturing a mold without using a pattern, comprising:
 a) providing a plurality of particulates;
 b) contacting at least a portion of a surface of the particulates with an activation agent for causing cross-linking of an organic binder material;

30

c) depositing the binder material onto a pre-selected portion of the particulates;

d) at least partially hardening the binder for forming a layer of the mold; and

5 e) repeating the steps (a)-(d) to form the remainder of the mold.

12) The method of claim 11 further comprising pouring a material, selected from a metal or a plastic, in a molten state, into the mold to form a part using the mold.

10

13) The method of claim 11 further comprising pouring a ceramic material into the mold.

14) The method of any of claims 11 through 13 wherein the
15 particulates are foundry sand particles.

15) The method of any of claims 11 through 14 wherein the particles have an average particle size of at least about 30 μm .

20

16) The method of claim 15 wherein the particles have an average particle size of at least about 90 μm to about 210 μm .

17) The method of claim 16 wherein the particles have an average particle size on the order of 140 μm .

25

18) The method of any of claims 1 through 17, further comprising forming a core in the mold.

19) The method of claim 1, wherein the binder material is free of a
30 thermoset resin.

20) A three dimensional form, comprising: a plurality of layers that include particles bound together by a binder material system that is at least two components, including an activation agent and a binder material, wherein

the binder material is not contacted with the particles prior to the activation agent.

21) The form of claim 20, wherein the layers are configured to form
5 an article selected from the group consisting of a casting mold, a die for molding, a die for thermoforming, an extrusion die, an orthopedic implant, a dental restoration, a vascular tissue, a sustained release drug form, a monochromatic prototype part, a multi-colored prototype part, a sculpture, a gradient index lens, a hollow part, an electronics component, a cutting tool,
10 and a metal matrix composite.

22) The form of claim 20 or 21, wherein the binder material is a cross-linkable material that cross-links in the presence of the activation agent.

15 23) A kit for preparing a three-dimensional form, comprising:
a) a first container including a binder material, and
b) a second container including a particulated material and an activation agent for the binder material.

20 24) The kit of claim 23 wherein the binder material is a cross-linkable material that cross-links in the presence of the activation agent.

25) A system for preparing a three-dimensional form, comprising:
a) a binder fluid dispenser containing a volume of binder fluid;
25 b) a work surface having a plurality of particles thereon that are contacted with an activation agent for the binder;
c) a mechanism for spreading particulated material;
d) a processor for commanding the binder fluid dispenser to dispense the binder fluid according to data from a computer-derived model,
30 wherein the binder fluid dispenser and the work surface are adapted for translation relative to each other in three dimensions.

26) The system of claim 25 wherein the binder fluid is a cross-linkable material that cross links in the presence of the activation agent.

- 27) The system of claim 25 or 26 wherein the binder fluid dispenser includes a drop-on-demand fluid dispenser.
- 5 28) The system of any of claims 25 through 27, wherein the binder fluid dispenser employs piezoelectric jets, a continuous jet spray, an intermittent jet spray, dispenses through a mask, includes a single dispensing nozzle, includes a plurality of dispensing nozzles that are clustered together, includes a heated nozzle, includes a plurality of dispensing nozzles that are
10 spaced apart, or combinations of at least two of the foregoing characteristics.
- 29) The system of any of claims 25 through 28 wherein the work surface is provided as a vertically translatable surface of a gantry.
- 15 30) The system of any of claims 25 through 29 wherein the spreading mechanism includes an oscillating blade, a doctor blade, a counter rotating roller, or a combination thereof.
- 20 31) The system of any of claims 25 through 30 further comprising a continuous mixer, a batch mixer or a combination thereof, for contacting the particles with the activation agent.
- 32) A method for making a three dimensional form, comprising the steps of:
- 25 a) providing a plurality of particulates;
- b) contacting at least a portion of a surface of the particulates with a multiple-component binder material system including a binder material as one of the components;
- c) at least partially hardening the binder for forming a layer of the
30 three-dimensional form;
- d) repeating the steps (a)-(c) to form the remainder of the three-dimensional form; and
- e) re-claiming unbound particulates, said unbound particulates being free of binder material.

33) The method of claim 32 wherein the particulates comprise foundry sand.

5 34) The method of claim 32 or 33 wherein the binder material is selected from the group consisting of phenol resin, polyisocyanate, polyurethane, epoxy resin, furane resin, polyurethane polymer, phenolic polyurethane, phenol-formaldehyde furfuryl alcohol, urea-formaldehyde furfuryl alcohol, formaldehyde furfuryl alcohol, peroxide, polyphenol resin,
10 resol ester or mixtures thereof.

 35) The method of claim 34, wherein one component of the multi-component binder material system is an activation agent selected from an acid, an amine, an ester or a combination thereof.

15

 36) The method of claim 32 wherein the resulting form is an article selected from the group consisting of a casting mold, a die for molding, a die for thermoforming, an extrusion die, an orthopedic implant, a dental restoration, a vascular tissue, a sustained release drug form, a
20 monochromatic prototype part, a multi-colored prototype part, a sculpture, a gradient index lens, a hollow part, an electronics component, a cutting tool, and a metal matrix composite.

25

30